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Described is the synthesis of two spiro core segments of orthogonally arranged conducting systems. The final systems are to have a potentially conducting chain fused perpendicularly to a second potentially conducting chain via a sigma bonded network. These systems may be suitable for incorporation into future molecular electronic devices. One of the core segments synthesized is based on a thiophene conducting group and it is formed by a zirconium-promoted bis(bicyclization) of bis(diyne) systems. The second is a phenylene-based system which is derived from fluorene. Terminal bromide groups provide the linkage points for further extensions of the chains via palladium-catalyzed cross coupling methods.

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Approaches to Orthogonally Fused Conducting Polymers for Molecular Electronics¹

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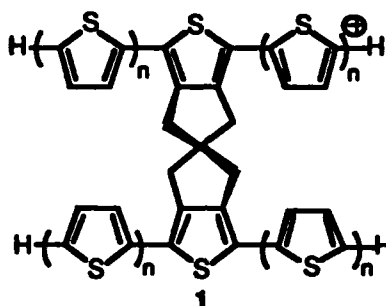
Abstract

Described is the synthesis of two spiro core segments of orthogonally arranged conducting systems. The final systems are to have a potentially conducting chain fused perpendicularly to a second potentially conducting chain via a sigma bonded network. These systems may be suitable for incorporation into future molecular electronic devices. One of the core segments synthesized is based on a thiophene conducting group and it is formed by a zirconium-promoted bis(bicyclization) of bis(diyne) systems. The second is a phenylene-based system which is derived from fluorene. Terminal bromide groups provide the linkage points for further extensions of the chains via palladium-catalyzed cross coupling methods.



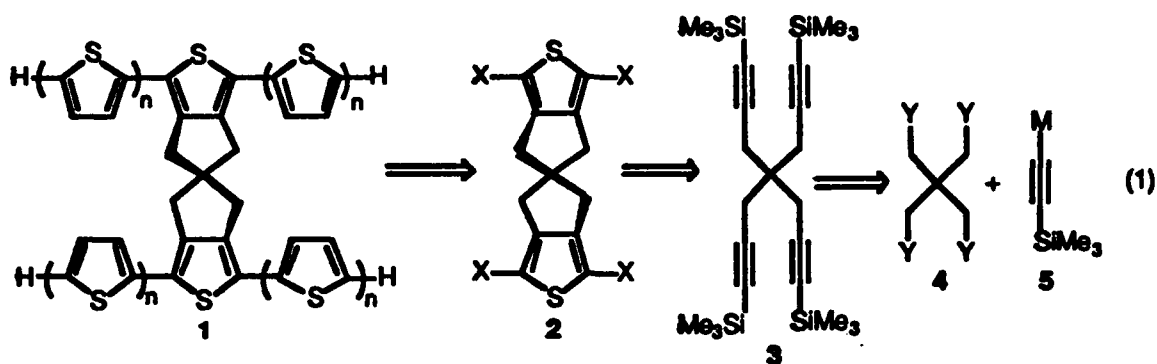
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Molecular electronics-based computing instruments possess tremendous technological potential. There is the hope of developing single molecules that could each function as a self-contained electronic device. Thus, one can envision computing systems with molecular-sized electronic elements and operational efficiencies far exceeding that of present systems.³ Recently, Aviram of the IBM Corporation has suggested that molecules which contain a pro-conducting (non-doped or non-oxidized system, hence insulating) polymer which is fixed at a 90° angle via a non-conjugated sigma bonded network to a conducting (doped or oxidized system) should exhibit properties which would make it suitable for interconnection into future molecular electronic devices.⁴ These devices may be useful for the memory, logic, and amplification computing systems. The molecule 1 (in doped form) is an example of this pro-conducting/sigma/conducting type of molecule.

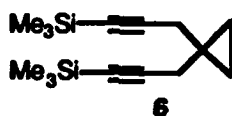


We have undertaken the synthesis of several molecules which fit the structural requirements of this electronic model. From the synthetic standpoint, several aspects are challenging. First, there must be a one spiro-fused junction separating two potentially conducting chains with a tetrahedral bonding atom at the center to maintain the 90° angle via a sigma bonded network. Secondly, all four conducting chains originating from the central segment must be *identical* in length. These requirements prohibit the use of any random polymerization methods. Initial reports suggested conducting chains ~50 Å long (from end to end rather than from end to core) would fulfill the model.⁴

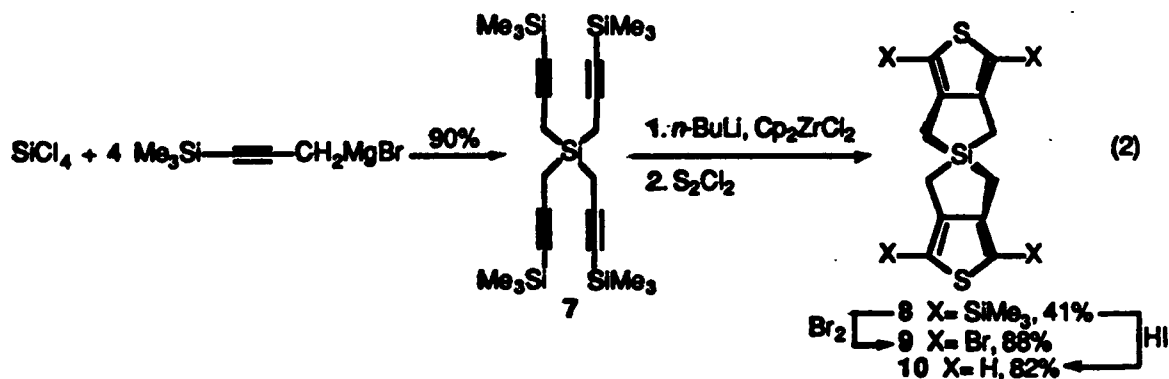
Our initial approach to these systems involved the synthesis of the key spiro core 2 from which we envisioned selective oligomerization to the target molecule 1. A retrosynthetic analysis is shown in eq 1.



Though substitutions on pentaerythrityl tetrahalides involves reactions on a neopentyl system, exhaustive substitution has been accomplished using oxygen, nitrogen, and sulfur nucleophiles.⁵ Attempted formation of 3 using 1-metallo-2-(trimethylsilyl)acetylenes 5 and pentaerythrityl tetrahalides and tosylates 4 proved to be very difficult even though we tried numerous coupling procedures ($M = \text{MgBr}$, Li , ZnCl , Cu , AlR_2 with and without Pd and Ni catalysis). In several cases, we obtained the cyclopropyl system 6.⁶ In an effort to overcome these difficulties while

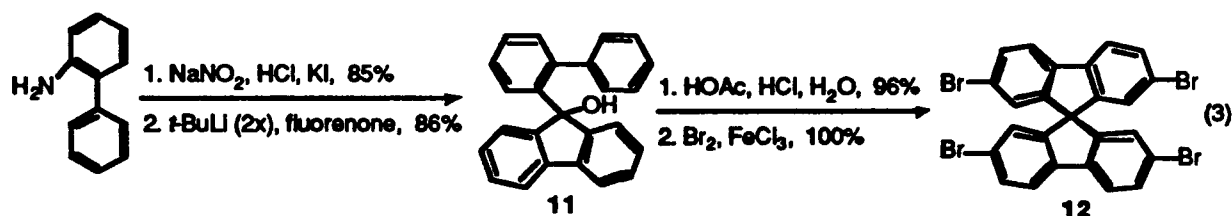


maintaining the required sigma bonded tetrahedral spiro junction, we turned our attention to the use of silicon as the central atom. Accordingly, treatment of SiCl_4 with the silyl protected propargyl Grignard reagent cleanly afforded the tetra(alkyne) 7.⁶ Treatment of 7 with a zirconocene equivalent, generated *in situ* from zirconocene dichloride and butyllithium, and quenching with sulfur monochloride afforded the trimethylsilyl-spiro core 8 (eq 2).^{6,7} To our knowledge,



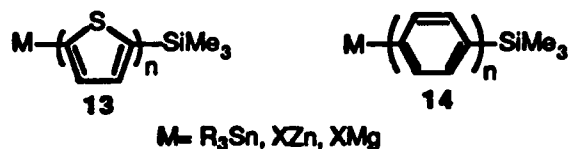
use of this group IVA coupling procedure for a *bis*(bicyclization) has never before been demonstrated. The trimethylsilyl core (8) was converted to the tetrabromide (9) and parent core (10) under electrophilic substitution conditions.^{6,8} Remarkably, no attack on the pseudo allylic central silicon atom was observed.

Likewise, we have synthesized another key core segment based on a *p*-polyphenylene⁹ conducting unit which fits the general electronic architectural requirements. Conversion of 2-aminobiphenyl to the corresponding iodide under Sandmeyer¹⁰ conditions followed by lithium halogen exchange and quenching with fluorenone afforded the alcohol 11. Acid treatment to close the spiro system¹¹ followed by reaction with bromine and FeCl₃ gave the tetrabromide 12 in excellent yields (eq 3).⁶ Bromination occurred only at the positions para to the second ring in

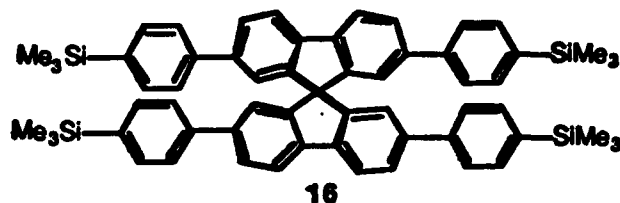
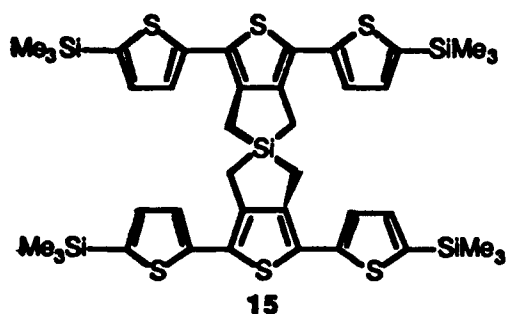


the chain as one would expect by resonance stabilization arguments of the ionic intermediate. It is imperative that the bromination take place at the para position since a 4-substituted moiety is essential to afford a highly conducting system.⁹

With two key core units in hand, we then addressed methods to selectively and equally extend the chains in all four directions. Coupling 9 and 12 with 13 and 14, respectively, using transition metal catalysis¹² would allow for the selective introduction of a known number of units.¹³ Additionally, the terminal trimethylsilyl



group in 13 and 14 would allow for selective bromination at those sites and, hence, a position for further coupling if necessary.^{8a} Accordingly, treatment of 9 with 13 ($M = Bu_3Sn$, $n = 1$) in the presence of catalytic Pd(PPh₃)₄ afforded 15 in 41% yield. Likewise, treatment of 12 with 14 ($M = ClZn$, $n = 1$) under similar catalytic conditions afforded 16 in 40% yield.⁶



Use of 3-substituted thiophenes for connection to both 9 and 12 is also being investigated to help in solublizing these systems.^{13,14}

Clearly, the efficiency of these coupling reactions must be optimized and the chain lengths further extended. However, these synthetic approaches demonstrate the power of modern synthetic methods to allow for the construction of macromolecules with the extremely specific architectural requirements necessary for the construction of the future molecular-electronics-based computing machine.

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